This is a progress report; it is therefore subject to revision and correction and should not be quoted nor referred to without the written permission of the author.

Department of Chemical and Metallurgical

Engineering,

University of Tennessee

Knoxville, Tennessee

SEMI-ANNUAL PROGRESS REPORT,

ON THE APPLICATION OF DIFFUSE

X-RAY SCATTERING TO THE STUDY

OF THE STRUCTURE OF BINARY

ALLOYS

September 1, 1966 - February 28, 1967

NASA Grant NGR-43-001-018

Submitted to

National Aeronautics and Space Administration

Washington, D. C., 20546

Submitted by

J. E. Spruiell

I. INTRODUCTION

The research in progress under this grant (NASA Grant NGR-43-001-018) consists of an experimental and theoretical investigation of the relationship between the local atomic arrangements in metallic solid solutions and the physical, mechanical, and thermodynamic properties of the solid solutions. The present report outlines the status of our research relative to the local atomic arrangements in Ni-Pd alloys. Much of this research was conducted during the period September 1, 1966 to February 28, 1967.

The Ni-Pd system has generally been regarded as forming a complete series of solid solutions in which no superlattices or intermediate phases are formed (1). The evidence for the absence of superlattices in the system is the x-ray diffraction work of Hultgren and Zapffe (2) on Ni-Pd alloys annealed at low temperatures. They could find no evidence in their Debye-Scherrer patterns for the existence of ordering or for a miscibility gap which had been suggested by Fraenkel and Stern (3).

In recent years, however, several Russian investigators (4,5,6,7,8,9,10) have noted anomalous electrical and magnetic behavior at the stoichiometric compositions $NiPd_3$ and Ni_3Pd which they attribute to the existence of superlattices at these compositions. In a very recent paper (11), Akira Nagasawa also claimed the existence of superlattices at $NiPd_3$ and Ni_3Pd based on evidence obtained through an electron diffraction study of thin, vapor deposited, Ni-Pd films.

Furthermore, the relative thermodynamic properties of Ni-Pd alloys have been measured by Bidwell and Speiser (12) in the temperature range 700-1200°C. In order to assess the configurational contribution of the mixing process in Ni-Pd alloys, the magnetic, electronic, and lattice

vibrational contributions to the thermodynamic properties were taken into account, and crudely estimated. After subtracting these non-configurational contributions, the remaining excess entropy and enthalpy of mixing were negative and asymmetric toward the Pd-rich end. They concluded that, if these quantities are interpreted in terms of quasichemical theory, Ni-Pd alloys, particularly Pd-rich solutions, possess short-range order at elevated temperatures and possibly long-range order at low temperatures.

In order to obtain a more direct and quantitative verification of the results suggested by Bidwell and Speiser's interpretation of their thermodynamic data and to gain a more complete understanding of the local atomic arrangements and their relation to the physical and thermal properties of Ni-Pd alloys, measurements of the diffuse x-ray scattering from three Ni-Pd single crystals were carried out. The results were very surprising in that the expected superlattices and short-range order were not observed.

II. EXPERIMENTAL PROCEDURE

Three Ni-Pd single crystals with compositions corresponding approximately to 25, 50, and 75 at. % Pd were grown by the Bridgman technique using the equipment described in a previous status report (13). The crystals were grown with growth rates of the order of 1-inch per hour in a vacuum of approximately 10^{-5} torr, and they were subsequently homogenized by holding them for approximately 100 hours at 1100°C. Both metallographic and x-ray diffraction evidence (Debye-Scherrer patterns of filings and Laue patterns) indicated that no macroscopic segregation or coring remained in the crystals after the homogenization treatment.

The orientations of the crystallographic axes were located by the back-reflection Laue technique and 1/8-inch thick discs were cut from the crystals with an approximately (210) face. These discs were heat treated and metallographically polished prior to mounting on the x-ray diffracto-meter inside a cryostat and vacuum chamber.

Diffuse scattering measurements were made using CuKα radiation monochromated by a doubly bent LiF crystal and Ni-Co balanced filters. The intensity was counted for 60 seconds with each filter at points on the h_1h_2O plane of reciprocal space separated by 2 degrees in 2θ and χ. An NaI scintillation counter equipped with pulse height discrimination detected the radiation scattered from the specimen.

The intensity measurements were converted to absolute units by comparison with the intensity scattered from polystyrene, C_8H_8, at a scattering angle 2θ of 100 degrees. The Compton scattering was also calculated and substracted from the data.

III. RESULTS AND DISCUSSION

Several measurements of the diffuse scattering from the Ni-25, 50, and 75 at.% Pd crystals were made. A list of the sample conditions and type of data collected is presented in Table I.

Figures 1, 2, and 3 show diffuse intensity distributions on the h_1h_2O plane of reciprocal space for the 25, 50 and 75 at.% Pd crystals, respectively, after these crystals were furnace cooled under vacuum from 1100°C. These measurements correspond to conditions a, d, and g in Table I.

TABLE I

Diffuse Scattering Measurements Completed for Nickel-Palladium System

| Crystal		Heat Treatment of Sample	Range of Data Collected
Ni-25 at.% Pd	(a)	Annealed 118 hrs. at 1160°C, furnace cooled to room temperature.	h_1h_2O plane at r. t.
	(b)	Annealed 1 hr. at 950°C, furnace cooled to 750°C, annealed 8 hrs. at 750°C, quenched in r. t. water.	Few lines through the diffuse scattering peaks
	(c)	Annealed 11 hrs. at 980°C, quenched in r. t. water.	h_1OO , h_1h_1O lines
Ni-50 at.% Pd	(d)	Annealed 96 hrs. at 1100°C, furnace cooled to room temperature.	h_1h_2O plane at r. t. and at 86°K.
	(e)	Annealed 2 hrs. at 700°C, quenched to r. t. water	Same as (b)
	(f)	Annealed 4 hrs. at 950°C, quenched in r. t. water, annealed 132 hrs. at 550°C, quenched in r. t. water.	Same as (b)
Ni-75 at.% Pd	(g)	Annealed 142 hrs. at 1180°C, furnace cooled to room temperature.	h_1h_2O plane at r. t.
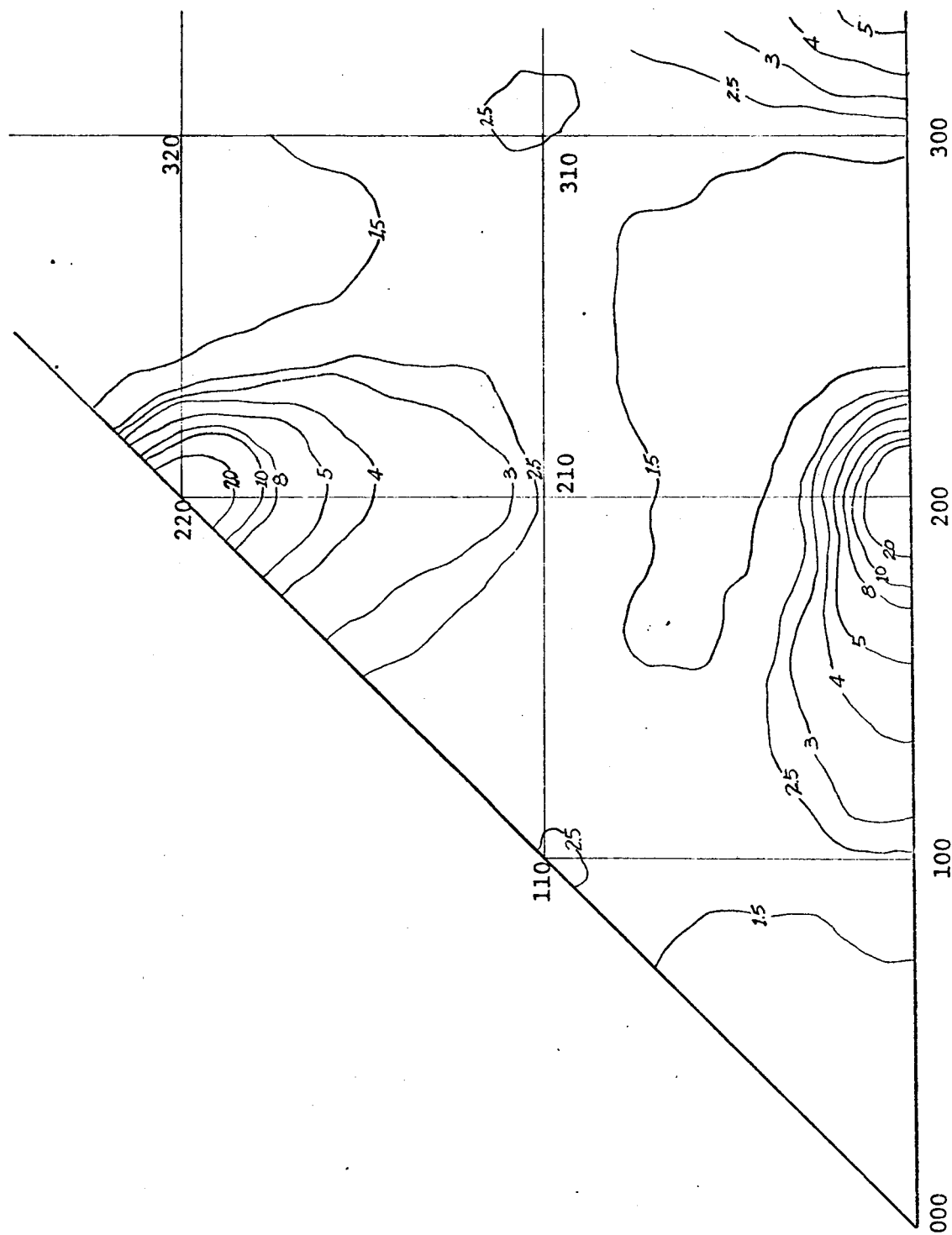
Fig. 1. Intensity distribution on the h_1h_20 plane of reciprocal space for a Ni-25 at.% Pd single crystal which has been furnace cooled from 1100°C. Intensities are given in units of $I/NM_AM_B(f_A-f_B)^2$.
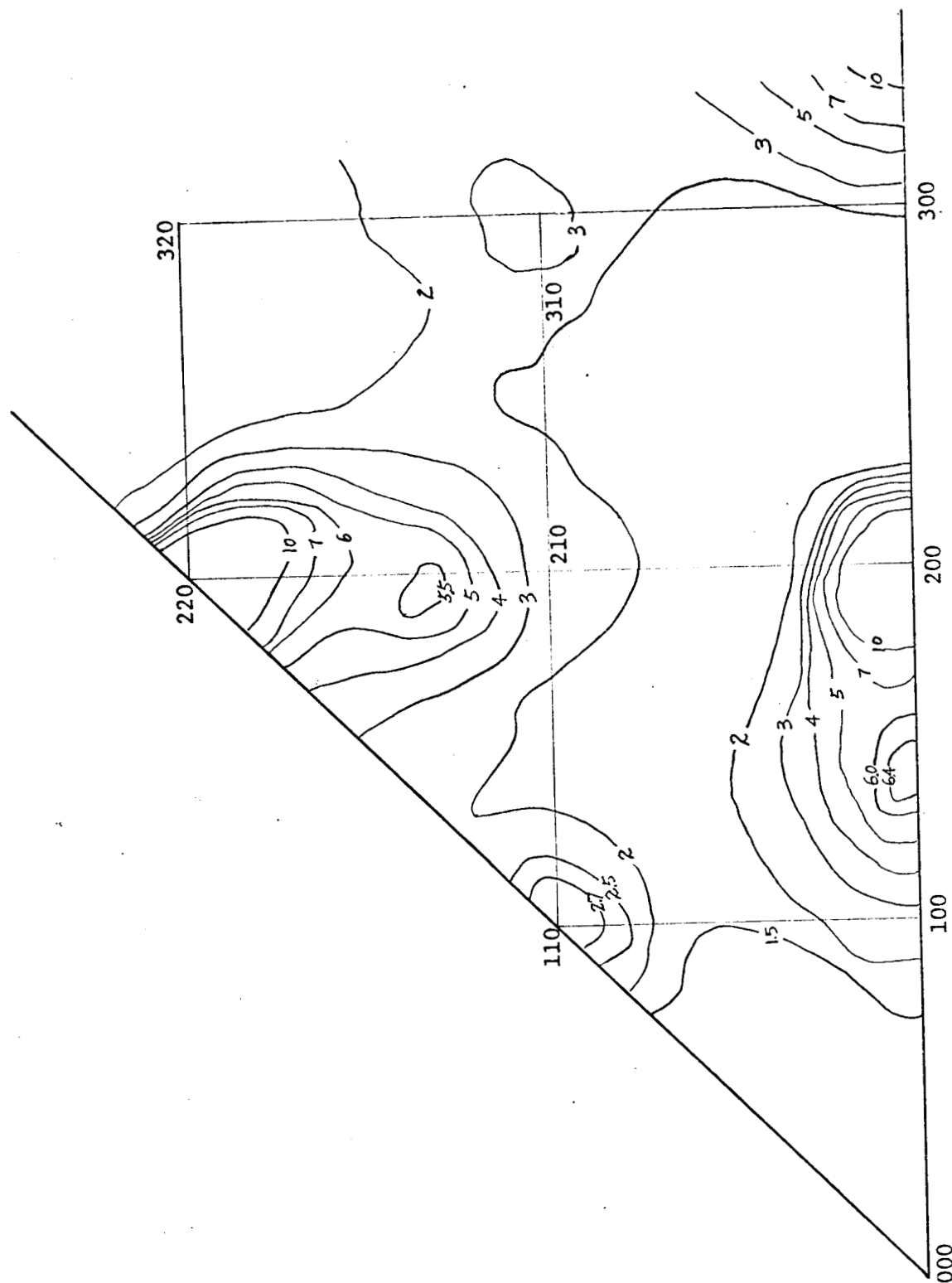
Fig. 2. Intensity distribution on the h_1h_20 plane of reciprocal space for a Ni-50 at.% Pd single crystal which has been furnace cooled from 1100°C. Intensities are given in units of $I/NM_AM_B(f_A-f_B)^2$
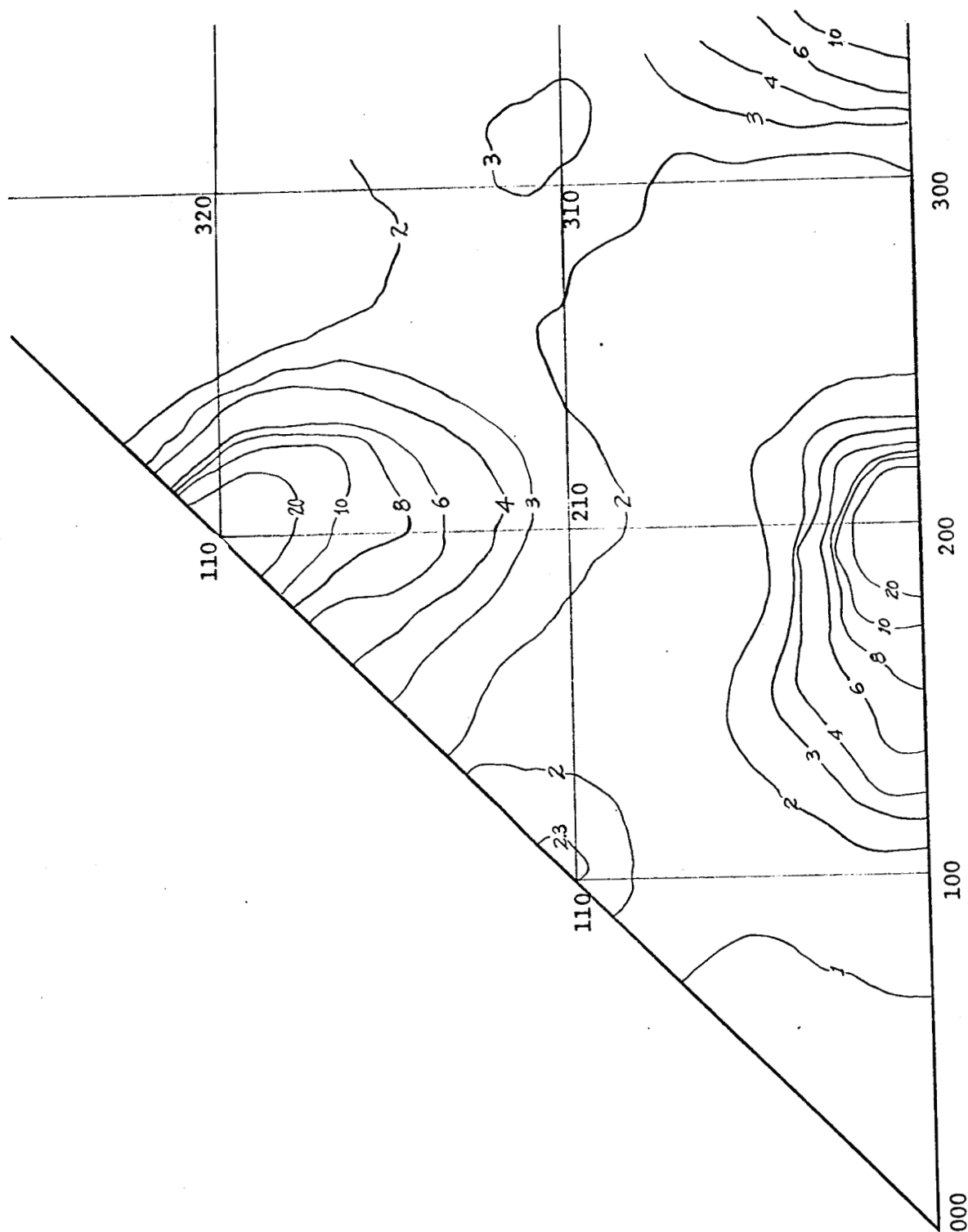
Fig. 3. Intensity distribution on the h_1h_2O plane of reciprocal space for a Ni-75 at.% Pd single crystal which has been furnace cooled from 1100°C. Intensities are given in units of $I/NM_AM_B(f_A-f_B)^2$.

The diffuse intensity distributions of Fig.'s 1, 2, and 3 are nearly the same, a fact which implies that the three alloys have similar structures. The main differences between the three figures lies in the occurrence of a distinct maximum in the diffuse scattering near the (1.4,0,0), and (2,2.4,0) positions in Fig. 2, while only a gradual increase in the intensity is observed in Fig.'s 1 and 3 as the Bragg peaks are approached.

The effects of the heat treatments investigated so far were slight. No significant change in the intensity distribution of Figure 1 was observed due to treatments b and c of Table 1, although treatments e and f removed the distinct maxima occurring at the positions (1.4,0,0) and (2,2.4,0) in Fig. 2, making the diffuse intensity distribution after treatment e and f appear more like those in Fig.'s 1 and 3.

A schematic representation is presented in Fig. 4 of the diffuse intensity distribution throughout reciprocal space and as inferred from the two-dimensional data. It is apparent from this figure that the small peaks near the (110) and (310) positions in Fig.'s 1, 2, and 3 are caused by the intersection with the h h 0 plane of the football shaped intensity lobes extending down from the (111) and (311) Bragg peaks.

There is no evidence in Fig.'s 1, 2, or 3 for any peaking of the diffuse intensity at positions such as (100), (210) or (300) although the intensity is not negligible at these positions due to overlap of the maxima centered near (1.4,0,0)(2,1.4,0) and (3.5,0k0). These facts would seem to imply that the scattering is not due to short-range order, since even a slightly
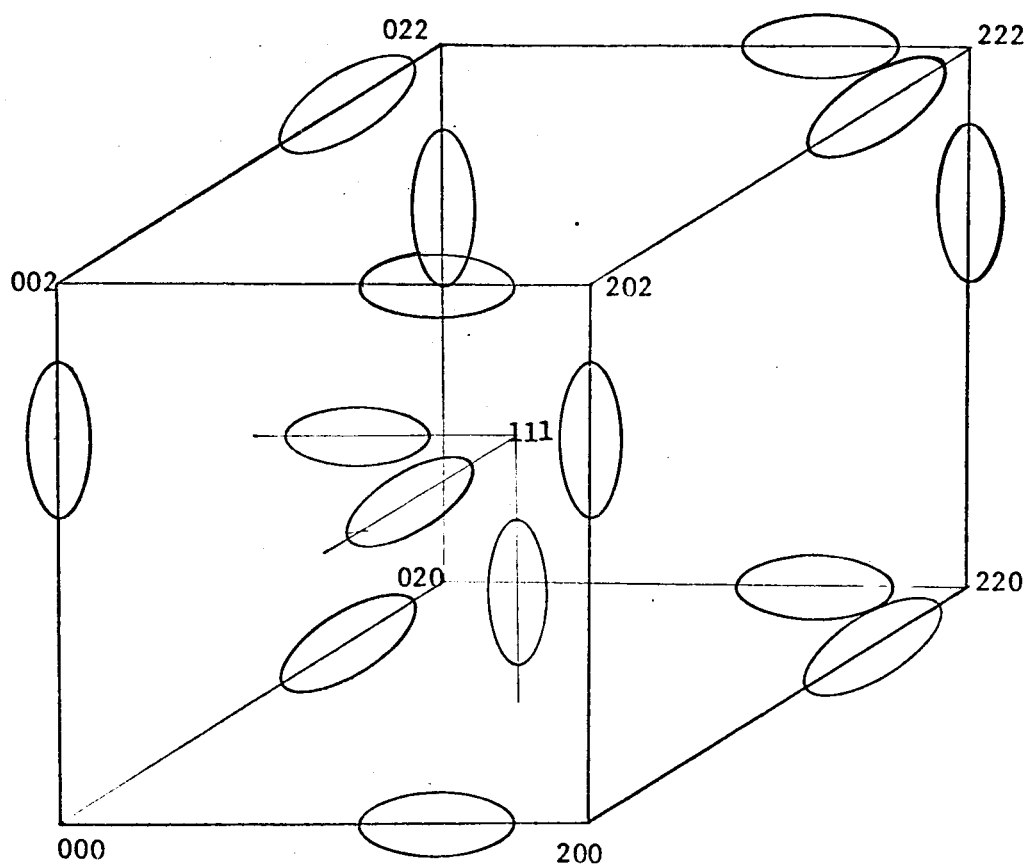
Fig. 4. Schematic representation of the diffuse intensity
         distribution in three-dimensional reciprocal space
         for Ni-Pd single crystals.

negative value of the first neighbor local order parameter, α_{110}, would produce weak diffuse maxima of equal intensity at all positions of mixed (odd and even) indices.

Assuming that the diffuse scattering distributions shown in these figures are not due to short-range order, what could be their origin? In general we may say that a large atomic size effect, or clustering, or both could cause the modulations of the intensity observed on the data of Fig.'s 1, 2, and 3.

Furthermore, only the atomic size effect can produce an asymmetric distribution about a Bragg peak such as is observed about the (200). Thus there is definitely a large atomic size effect indicated by the data. It is not likely, however, that the distributions are caused by the size effect alone due to the fact that the diffuse scattering actually peaks at positions such as (1.4,0,0)(in the case of Fig. 2).

The following model qualitatively explains the intensity distribution illustrated by Fig. 4. The Ni-Pd solid solutions contain composition modulations along <100> directions. This is a form of clustering in which a Ni-rich region parallel to a {100} type plane is followed by a parallel Pd-rich region and etc. The composition modulations appear to be one-dimensional rather than three-dimensional (such as might be predicted for spinodal decomposition (14)). This statement is based on the fact that 110 harmonics of the composition modulation would result in intensity maxima near the (1.4,0.6,0) and (1.4,1.4,0) positions if the composition modulation were three-dimensional. The absence of intensity peaks at these positions indicates that the modulations are probably one-dimensional. The crystal may be thought of as subdivided into three types of domains. Within each

domain the composition modulates along a specific [100] direction; domains in which composition modulations occur along [100], [010], or [001] occur with approximately equal probability. A large atomic size effect also occurs and is responsible for the asymmetric intensity distribution about the Bragg reflections. The exact nature of this size effect is not yet clear.

Based on the position of the diffuse maxima it is possible to estimate the average wavelength of the composition modulations along the [100] directions. This estimate gives an average wavelength of about 6.2 $\overset{o}{A}$ for the slow cooled, Ni-50 at.% Pd crystal. This means that on the average there are about 1.67 Ni-rich (100) planes followed by 1.67 Pd-rich (100) planes in the composition modulation. The other compositions and heat treatments appear to have modulations of somewhat longer wavelength since the diffuse maxima are somewhat nearer the Bragg peaks. However, it is difficult to say precisely what the wavelengths are in these cases because the diffuse maxima overlap so strongly with the Bragg reflections. At the present time we have made no estimates of the amplitudes of the composition modulations.

Some electrical resistivity measurements have been made on alloys containing 25, 50 and 75 at.% Pd. As shown in Fig. 5 these measurements indicate that the resistivity of previously annealed Ni-Pd alloys increases with cold work; i.e., there is no K-state formation in these alloys. Hence the clustering effects observed in these alloys do not lead to K-state behavior.

Furthermore, the observed clustering behavior together with the quasichemical theory predicts a positive heat of mixing (for the configurational part). This result does not agree with Bidwell and Speiser's (12) interpretation of their thermodynamic data. We plan to consider the
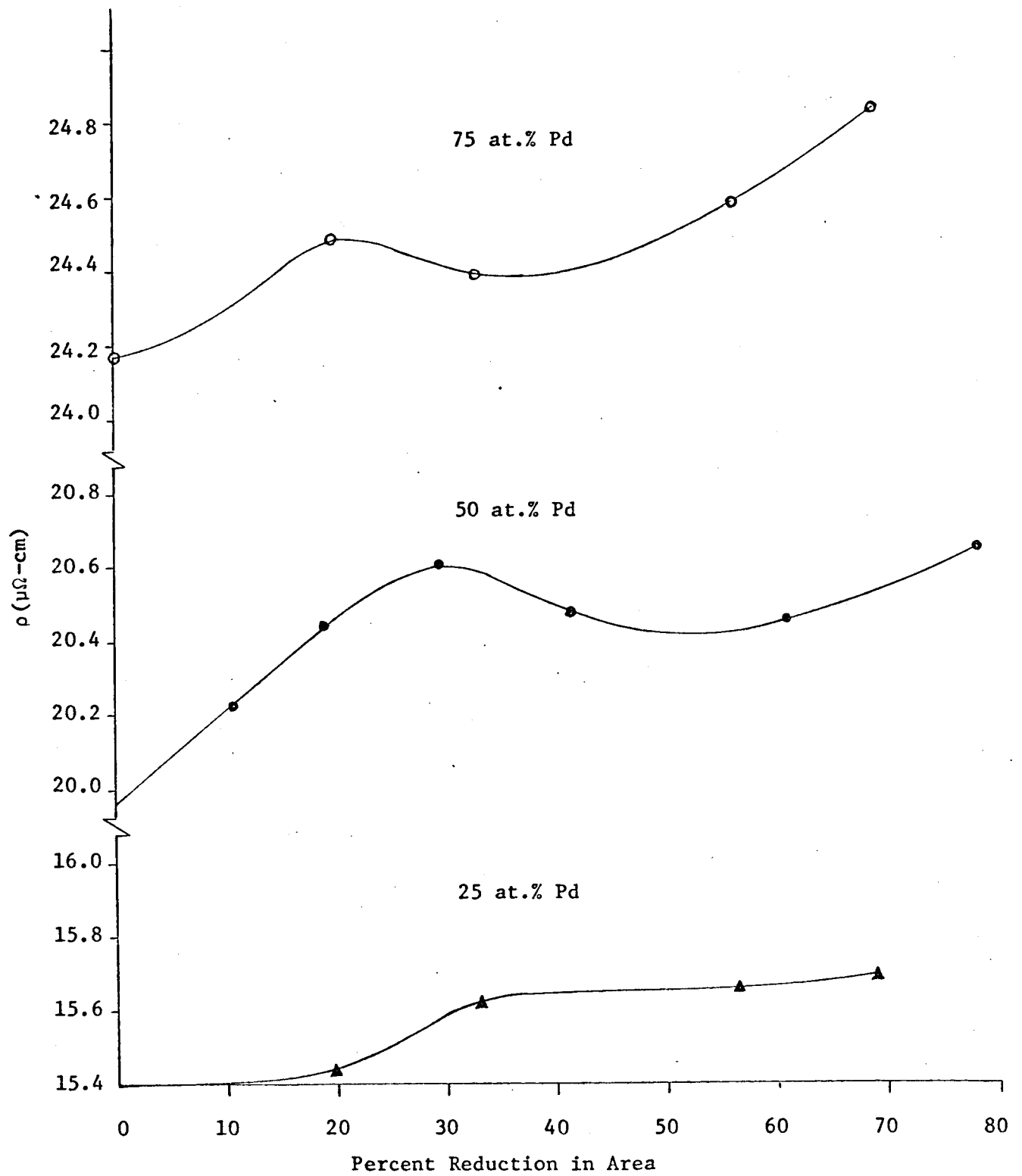
Fig. 5. Resistivity as a function of cold work for Ni-Pd alloys.

implications of these results more fully at a later date, after a quantitative separation of the diffuse scattering into its component parts.

The differences between our results and those of Nagasawa (11) deserve investigation. We plan to investigate these differences by thinning some of our bulk samples and examining the electron diffraction from them in the electron microscope. It may be that the results obtained by Nagasawa are peculiar to Ni-Pd alloys formed by vapor deposition.

LIST OF REFERENCES

1. Hanson, M. and Anderko, K., Constitution of Binary Alloys, McGraw-Hill, New York (1953).

2. Hultgren, R. and Zapffe, C., Trans. AIME, 133, 58(1939).

3. Fraenkel, W. and Stern, A., Z. Anorg, im Allgemeine Chem., 166, 164 (1927).

4. Annaev, R. G. and Yazliev, S., Izvest. Akad. Nauk Turkmen, SSR, No. 6, 3 (1957).

5. Mvalikgulyey, G., Izvest. Akad. Nauk Turkmen, SSR, No. 1, 164 (1959).

6. Permanova, M. K., Izvest. Akad. Nauk Turkmen, SSR, seri. Fiz.-Tekh., Khim. i Geol. Nauk No. 4, 35 (1961).

7. Yazliev, S., Izvest. Akad. Nauk Turkmen, SSR. SERI. Fiz.-Tekh., Khim. i Geol. Nauk No. 6, 33 (1961).

8. Yazliev, S., Inzvest. Akad Nauk Turkmen, SSR, seri. Fiz.-Tekh., Khim. i Geol. Nauk No. 4, 14 (1961).

9. Annaev, R. G., Nyalikgulyev, G., and Orazsakjatov, A., Izvest. Akad. Nauk Turkmen, SSR, seri. Fiz.-Tekh., Khim.

10. Annaev, R. G., Myalikgnlyaev, G., and Yusupov, T. M., Izvest. Akad. Nau, Turkmen, SSR, seri. Fiz-Tekh., Khim. i Geol.

11. Nagasawa, A., J. Phys. Soc. Japan, 21, 1215 (1966).

12. Bidwell, R. L. and Speiser, R., Acta Met., 13 (2), 61 (1965)

13. Spruiell, J. E., Semi-Annual Progress Report for NASA Grant NGR-43-001-018 for peirod September 1, 1965 - February 28, 1966.

14. Hilliard, John E., Industrial and Engineering Chemistry, 58, 19-25 (1966).